

## **SUSTAINED RELEASE PEST CONTROL PRODUCTS AND THEIR APPLICATION**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is a continuation-in-part of application serial no. 09/993,611 filed on November 27, 2001; which is a continuation-in-part of application serial no. 09/347,704 filed on July 3, 1999, now U.S. Patent No. 6,322,803, the disclosures of which are expressly incorporated herein by reference.

### **STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH**

Not applicable.

### **BACKGROUND OF THE INVENTION**

The present invention relates generally to a method for applying and delivering pesticides, insecticides, and repellents to structures, surfaces of structures, and materials important to commerce and industry, and more particularly to the use of colloidal clays for adsorbing pesticide(s) or other bioactive active chemicals for producing polymeric coatings having extremely long useful lives of sustained release of active ingredients.

Wood and wood products utilized in a variety of construction applications are frequently structurally degraded by the action of termites, ants, other boring insects, and wood decaying microorganisms. Typically, these wood degrading and decaying organisms migrate to wood structures via the surrounding soil or water. This migration may occur whether the structures rest upon concrete foundations, such as in wooden building construction; are in direct contact with the soil, for example fence posts, utility poles, railroad cross-ties, wooden supports, and like structures; or are in the water, such as boats, piers, pier pilings, wooden docks, or other supports. Wood and wood-containing products include, *inter alia*, glued wood products such as, for example, plywood, particleboard, oriented strand board (OSB), medium density fiberboard (MDF), laminated veneer lumber (LVL), laminated beams, and a variety of other engineered wood products. Paper products (especially paperboard and kraft paper) also are subject to degradation by organisms that attack wood. Outdoor furniture also is subject to wood degrading and decaying organisms. In the marine

context (including for example, pleasure and commercial craft for use on lakes, rivers, and oceans), the structures additionally may be manufactured from fiberglass, various plastics, metals, ceramics, and other materials.

Present methods of preventing or retarding the advance of these wood  
5 degrading organisms include soil treatment with pesticides and repellent chemicals, treatment of the wood with chemicals, and fumigation wherein the entire structure may be sealed and a pesticide pest repellent released. Both soil and fumigation type treatments may release the pesticide to the surrounding atmosphere and/or the pesticide may move to ground water where it may harm human beings or other living  
10 organisms. Disadvantages of these methods of treating soil and/or fumigating include, *inter alia*, potential ecological and human health concerns, as well as the limited time until the fumigant or soil concentration is sufficiently reduced in concentration to permit ingress of wood degrading organisms.

Although many pesticides and repellents are known to be effective against  
15 the action of wood destroying organisms, their effectiveness often declines over time as they are dissipated into the surrounding environment (soil, water, or atmosphere) or are degraded, for example, chemically or biologically. To retain their effectiveness, these insecticides must be repeatedly applied at regular intervals ranging from every few days to every few months to every few years. Alternatively, if  
20 the pesticides and repellents are applied in sufficient quantity to be effective over an extended period of time, the ecological and human health related concerns associated with these chemicals and their unpleasant odors are exacerbated. Furthermore, with the banning of certain chemicals and the introduction of safer shorter half-life compounds, even large amounts of many of these pesticides and  
25 repellents may be required over a relatively short time periods, and they will need to be reapplied more often.

A further disadvantage of conventional application methods is that the concentration of pesticides and repellents resulting from a single application starts out well above the minimum concentration necessary for effectiveness, but  
30 decreases rapidly. Within a relatively short period of time the concentration drops below the minimal effective level necessary to maintain a barrier to the invasion of wood compromising organisms.

To overcome these problems, a number of techniques for the controlled release of chemicals, such as insecticides, have been proposed. These methods employ polymer matrices and microcapsules used to contain insecticide and allow the slow release of the pesticides and repellents over extended time periods. One such scheme is found in U.S. Patent No. 4,400,374, which discloses the use of polymer matrices generally made of polyethylene, polypropylene, ethylene vinyl acetate, polyamide, polystyrene, polyvinyl acetate, or polyurethane to control the release of insecticides such as the insecticide commercially available under the trade name DURSBAN. The polymer matrices disclosed in U.S. Patent No. 4,400,374, incorporate a porosigen and a porosity reducing agent, which upon contact with soil moisture or an aqueous environment dissolves the matrix. Similarly, U.S. Patent No. 4,405,360 proposes a polymer release matrix, which can be composed of polyamide, polyurethane, polyethylene, polypropylene, polystyrenes, or other polymers. The control release mechanism works in combination with a porosigen to release a herbicide in a moist environment. A disadvantage of both of these methods is the necessity of sufficient moisture to dissolve the matrix. Periods of dryness, while extending the life of the matrix, results in a decrease in the insecticide concentration, thereby permitting insects to have access to the wooden structure. In addition, the longevity of the matrix is variable and dependent upon moisture content.

U.S. Patent No. 4,435,383 proposes the use of a controlled release mechanism for insecticides including carbamates, organothiophosphates, organophosphates, perchlorinated organics, and synthetic pyrethroids. The release mechanism comprises a hydrophobic barrier that is a polymer prepared from styrene and/or methyl styrene in combination with a monomer selected from one or more unsaturated mono- or di-carboxylic acids. U.S. Patent No. 5,860,266 proposes the preparation of construction sites with plastic sheets impregnated with an insecticide.

U.S. Patent No. 4,282,209 proposes a process for the preparation of insecticide-polymer particles. The insecticide, methomyl, is used to control insects, which attack tobacco, cotton, or other agricultural crops. Methomyl is dissolved into polymers, such as polyamides, urethanes, or epoxies, to provide extended residual insecticidal activity. U.S. Patent No. 4,235,872 proposes the use of slow-release

insecticide microcapsules having a core of methomyl surrounded by a cover of all-aromatic, un-crosslinked polyurea to protect vegetables, field crops, and fruit crops.

U.S. Patent No. 4,198,441 proposes the use of insecticides, such as chlorpyrifos (DURSBAN) in a controlled release matrix comprising an organopolysiloxane, a hydrolyzable silane, and a hydrolyzable organic titanium compound. U.S. Patent No. 4,160,335 proposes a mode of dispersing insect control substances by applying stripes to sheets of cellophane. The insect control substance, which can include DURSBAN, is placed in a polymer as well.

Australian patent AU-B-82443/91 proposes to use two sheets of plastic drawn from supply rolls, wherein the upper face of the lower sheet and the lower face of the upper sheet are drawn past respective coating rollers which apply a coating of pesticide (e.g., permethrin) in a volatile solvent to the faces of the sheets. The coated faces of the sheets are brought together by passing them between compressive rollers. The coated and pressed sheets are laid under building foundations or placed around trees or plants to prevent termite attack. Disadvantages of this product and method include (1) delamination permits rapid escape of the coating, and (2) the coating is not integral to the sheets, thereby permitting faster diffusion through the sheets and limiting the effective life.

Coated granules have a pesticide absorbed onto a matrix, such as clay, and then coated with cross-linked resins which helps slow the release rate. Clay loses or releases pesticide over a short period of at most a few weeks.

In U.S. Patent No. 5,801,194, a controlled release device is disclosed, which incorporates insecticide into polymer materials to form a device, which then may be placed in and around wooden structures to form an effective exclusion zone lasting several years or more. The reported extended effectiveness is accomplished by using of low volatility insecticide within a high-density polymer, the combination having a low release rate of the insecticide. While the '194 patent does describe a device that provides long lasting protection against insect penetration, the application of this device to either new or existing structures requires the manual placement of the device in and around those structures. The application of the device in this manner may be time consuming, labor intensive, and expensive. In one embodiment of the '194 patent, the controlled release device is placed into a polyurethane foam to

allow the spray application of the device to wooden structures. While this approach does lessen the labor, and thus the cost associated with placing the device in contact with the structures that need to be protected, it does have other drawbacks. For example, at the time the device is applied to the structure, the insecticide is not  
5 adequately dispersed throughout the volume of the polyurethane foam. This results in a lack of protection from invasive insects during the time period required for the insecticide to permeate the polymer and infiltrate the foam. To overcome this drawback, the '194 patent also proposes combining the low volatility insecticide within a high-density polymer with a more volatile insecticide within a low-density  
10 polymer which has a higher release rate. The drawbacks of this combined system include the potential harm to human and other life forms, which may occur as a result of their coming into contact with the more volatile insecticide.

Japanese Patent 62236937 proposes the use of a polyol/isocyanate/pesticide/microparticle solution that is painted or sprayed upon the  
15 surface of the foundation and the ground around the foundation. Inclusion of the microparticles creates gaps between the particles. The gaps are filled with the pesticide containing urethane polymer. Therefore, the urethane polymer containing the microparticles acts as a sponge and enables the release of the pesticide without trapping it. By the varying of the amount of microparticles, the applicator can change  
20 the rate of the pesticide release.

Thus, there exists a need for improved pesticide control agents for protecting wooden structures, which improved control agents provide immediate, as well as long lasting, protection from, *inter alia*, termites, ants, wood boring insects, and other wood destroying microorganisms. It is to such improved pesticide control agents that  
25 the present invention is addressed.

#### BRIEF SUMMARY OF THE INVENTION

A method for applying a barrier to a structure to prevent the infiltration of pest species includes providing a composition and associating the composition with the  
30 structure. The composition is formed from a polymer component having dispersed therein beads formed from colloidal clay and adsorbed pest control agent. Colloidal

clays (e.g., nano-clays) adsorb more pest control agent than do standard clays and release the adsorbed pest control agent at a slower rate than do standard clays.

The inventive composition forms a continuous or discontinuous layer thereof associated with the substrate to be protected. Preferably, then, the inventive composition is "film-forming" in that it forms a film, which preferably is continuous, recognizing that discontinuous films may provide adequate protection against certain pest species under certain circumstances. The inventive coating composition also can contain adhesive ingredients (e.g., low Tg resins, tackifiers, etc.) that render it a conventional "adhesive" in order to adhere well to certain structures and to even join two structural surfaces together. Moreover, by careful formulation, the inventive composition may exhibit the thixotropy and adhesive characteristics to render it a caulk or sealant and, thus, protect cracks in structures. Thus, the term "composition" is to be construed broadly for present purposes in that the inventive pest species barrier composition may perform as a coating on the structure to be protected even if it conventionally also may be termed an adhesive, caulk, sealant, or other designation.

With respect to the target organisms, the problem is that many organisms may be considered pests or benign under some circumstances, and pests under other circumstances. Frequently, a non-pest becomes a pest because it is in a location that humans define as inappropriate. The location may be acceptable, but the organism may be engaged in an activity that humans define as inappropriate. The damage done may be related to health, damage to property, esthetics, etc. Different cultures view certain organisms quite differently. Organisms fit into ecosystems, and exterminating a given species could have very undesirable overall results.

Thus, for present purposes, the invention defines "pest" in terms of:

1. species, and
2. location, and
3. activity to be controlled, and
4. damage to health/property/esthetics.

In the context of the present invention, the pest control agent emphasizes the location that prevents termites and other species from entering. A deer is a pest in this context, because a deer can facilitate a termite's breach of the barrier set up by the inventive system. A termite is not a pest if it is consuming dead wood in a forest.

Roaches, termites, fire ants as well as clams, Zebra Mussels, and snails all play important and critical roles in the ecosystem; but in the wrong place relative to our homes and businesses (e.g., like generating energy in power plants or protecting our landscaping from the deer browsing on it), they are then condemned as a "pest".

5 Thus, organisms are undesirable in the human definition based upon damage to structures, materials, or reduction in yield of a desirable crop species by the invasion of an undesirable pest species into the farmers' field.

For present purposes, then, the terminology "pest species" will be used to identify those (unwanted) organisms that are to be controlled. That is, "pest  
10 termites" are termites that attack buildings. "Pest deer" invade our urban space. When termites and deer occupy their natural habitats, they are not "pests" for present purposes.

Pest species, then, can include, *inter alia*, microbes, fungi, algae, bacteria, viruses, spores, insects, birds, animals (land and sea), rodents, and the like.  
15 Specific such pest species include, *inter alia*, termites, ants, boring wasps, deer, squirrels, mice, rats, mollusks (clams, oysters, mussels), and the like. For present purposes also, a "pesticide" is an active control agent or ingredient that repels, attracts, or kills pest species that are harmful to wood and wood-containing products. So long as the pest species does not invade the wood product, the control agent has  
20 accomplished its intended purpose, regardless of the mechanism of its action.

Advantages of the present invention include an inexpensive and convenient method for applying a pest control agent, which protects (e.g., wooden) structures. Another advantage is the protection of the wooden structures for relatively great lengths of time ranging from 1 to more than 30 years. A further advantage is that this  
25 protection is provided to the structures immediately upon the application of the pest control agent without allowing the release of the pest control agent to the environment in quantities that may have the potential to harm human beings or other desirable life forms which may come into contact with the wood destroying or wood decaying barrier. Yet another advantage resides in the unexpected adsorption capacity of colloidal clays and slow release rates, compared to standard sized clays.  
30 These and other advantages will be readily apparent to those skilled in the art based on the present disclosure.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention displays numerous features in that an active ingredient is adsorbed by the colloidal clay, which optionally may be coated with a barrier material that acts as membrane that allows the active ingredient to move to its surface. The bead (including for present purposes, *inter alia*, small globules, cylindrical bodies, platelets, and the like) is contained in a polymer (e.g., polyurethane) matrix that also acts as membrane that allows the active ingredient to move to its surface. The active ingredient on the surface controls (e.g., repels or poisons) selected (targeted) pest species that approach or touch the surface. The products of this invention provide sustained effective performance over many years. The products of this invention also can be applied by spraying, roller coating, other coating techniques, casting in place, pre-casting structures, caulk gun applied, and the like. These products also can protect cracks, gaps, and other irregular surfaces, in addition to floors, walls, and other conventional surfaces. To protect structures further, the composition can be admixed with soil, aggregate (e.g., pea gravel), sand, vermiculite, or perlite, and distributed in the soil around the structure to disturb an oft-used pathway of pests.

The colloidal state of the clay yields best performance in longevity and reduced pest control agent (e.g., Trifluralin) degradation, compared with standard clay, carbon black, and other fillers proposed in the prior art. The Examples will detail such performance.

The length and breadth of colloidal particles have all three dimensions within the size range of about 0.5 nanometers to about 3000 nanometers. Exfoliated Nanocor I.30 E (see Examples), for example, is far from spherical. It has a thickness of about 1 nanometer and other dimensions of about 1500 nanometers. It is a miniature "flatland". Broadly, then, colloidal particles for present purposes will range in size from about 20 microns to less than 1 nanometer. These dimensions result in extremely high average aspect ratios of around 200–500. For example, clays that have an aspect ratio greater than about 50, thickness less than about 10 nanometers, and other dimensions greater than about 0.5 microns, find use in the present invention.

Sources of the nano-clays include, for example, a smectite, that is



montmorillonite, or beidellite, or nontronite, or saponite, or sauconite, or mixtures thereof or minerals with high percentage of smectite, such as bentonite. Alternatively, the colloidal clays can be derived from a vermiculite or illite. The colloidal clay may be derived by melting a solid active ingredient and blending it with a smectite, for example, to make an expanded product, or by blending a fluid active ingredient with a smectite to make an expanded product.

Moreover, the small size and thickness means that one-gram contains over a million particles. Nano-clays take advantage of the effect of combining high aspect ratio and nanoscale size. Because nanometer-sized particles approach the scale of resin molecules, a very close encounter can be made between the two materials when the clay is properly surface modified. The particle-molecule interaction creates a constrained region at the particle surface, which immobilizes a portion of the resin matrix. With so many particles available for interactive association, the cumulative percent of constrained polymer can become large. In nylon resin systems, for example, the constrained region exceeds 60% of the total matrix.

The sorption process can use pest control agent (e.g., Trifluralin) vapor that contacts and permeates into the tiny clay particles. A fluidized bed process is especially convenient for loading the particles. However, molten or dissolved pest control agent (e.g., Trifluralin) also can be used for loading. The loaded colloidal clay is incorporated into a polymeric (e.g., elastomer) matrix that is advantageously is a polyurethane polymer. Other polymeric materials include, *inter alia*, polyethylene, polypropylene, polybutenes, natural rubber, polyisoprene, polyesters, styrene butadiene rubber, EPDM, polyacrylates, polymethacrylates, polyethylene terephthalate, polypropylene terephthalate, nylon 6, nylon 66, polylactic acid, polyhydroxy butyrate, polycarbonate, epoxy resins, or unsaturated polyester resins.

The bead content of the system must contain enough active ingredient to release at a rate that is adequate to repel the target pest species for a period of time that meets the longevity goals. For example, if the release rate is one microgram/cm<sup>2</sup>/day for 30 years (ca. 11,000 days), then the beads must store at least 11 mg for each square centimeter of surface area. The concentration of active ingredient in the bead additionally must not exceed a threshold level that would cause barrier failure.

### **Durable Polyurethanes**

The polyurethanes that are useful in this invention are designed to overcome the environmental challenges by use of one or more of the following methods. Hydrolysis is a major challenge. The present invention reduces exposure to water required for hydrolysis by designing the surface of the product to be hydrophobic. 5 Therefore, very little water will stay in contact with the surface. Aromatic isocyanates are replaced with aliphatic or alicyclic isocyanates, and polyols that contain ester or ether linkages are replaced with aliphatic or alicyclic diols. These changes make the product much more durable. Other approaches to fight hydrolysis include use of 10 such drying agents as molecular sieves or silica to tie up water that does pass through the surface of the product.

As used herein, "polyurethane" and "polyurethanes" include and mean polyurethanes, polyureas, polyetherureas, polyisocyanurates, polycarbodiimides. Such polymers are prepared by polyaddition of nucleophiles (e.g., polyols, 15 polyamines, water) to form polyisocyanates that contain two or more isocyanate groups, and combinations thereof. As used herein, the term "monomer" includes all substances that react to form polyurethanes. These monomers may themselves be polymers or "prepolymers" which contain multiple nucleophilic groups or isocyanate groups. Even water can be used to make these polymers and is in this sense a 20 monomer. For example, when water is utilized in a reaction with a polyisocyanate to form a polyurea, it is included within the definition of monomers herein. The term monomer should also be understood to include blends of monomers.

The products of this invention will be used frequently to coat concrete, masonry, and like surfaces, which often can serve as pest species pathways to wood 25 and wood products, as well as the wood products themselves. Fresh concrete contains an excess of lime that makes it highly alkaline. The inventive pest species control product can be tailored to overcome this alkaline hydrolysis challenge by using the hydrophobic surface approach.

Microbes are major agents that cause hydrolytic or oxidative damage. 30 Therefore, the inventive pest species control product may include antimicrobial active ingredients, as well as other pesticides.

Rodents, deer, and other large pest species may gnaw on the object that the inventive pest species control product is designed to protect. In such circumstances, one of the active ingredients will be an irritant, such as powdered pepper or pepper extract. Alternatively, bitter-tasting substances, such as those used in denaturing ethyl alcohol, could be used.

Exposure to sunlight can trigger several types of environmental degradation. Photochemical oxidation attacks polyurethanes that are based on aromatic isocyanates especially. Therefore, aromatics are replaced with aliphatic or alicyclic ingredients. Polyetherdiols have ether linkages that are subject of oxidative degradation. These vulnerable ingredients are replaced by aliphatic or alicyclic diols. Alternatively, pigments and/or UV absorbers also can be used to reduce the effects of sunlight.

Structures that are to be protected over time spans of decades develop cracks due to mechanical stresses. These cracks could affect the performance of the products of this invention. The polyurethanes of this invention also can be tailored to have adhesive and elastomeric properties to reduce the occurrence and adverse effects of cracking.

### **Compositions Rich in Polyureas**

The sprayability and longevity needed for some applications of this invention cannot be attained with conventional polyurethane technology in which isocyanates are reacted only with polyols. The polymerization time is too long and the degree of crosslinking is not sufficiently high. In this invention, most or all of the polyol is replaced with amine-containing ingredients. In such cases the transport polymer will predominate in urea groups, rather than urethane groups. Alternatively, thiols could serve as the active hydrogen reactive groups in place of hydroxyl (polyol) groups.

Thus, one or more isocyanate ingredients such as toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), polymeric methylene diphenyl diisocyanate (PMDI), hexamethylene diisocyanate (HDI), or isophorone diisocyanate (IPDI) is reacted with a separate mixture comprising one or more amine-containing ingredients, such as, for example, 4,4'-methylene dianiline, 1,4-diaminocyclohexane, 2,4-diaminotoluene, 2,6-diaminotoluene, or 1,4-diaminohexane. The active

ingredient that may be incorporated into a colloidal clay bead is combined with this amine component. The amine formulation also can include some polyols, diols, and catalysts to adjust the physical properties (e.g., modulus) of the polymer, the rate of reaction, and to reduce unit costs. The reactants are kept separate in a two-  
 5 component spraying system until time for reaction because the gel time may be as little as 5 seconds. The spraying method disclosed in U.S. Patent No. 6,250,567 may be useful for this application.

The polymer made by this process contains mostly urea linkages, instead of mostly urethane linkages that are formed in conventional urethane polymers. Urea  
 10 linkages are more resistant to hydrolytic reactions that are the major causes of polymer degradation. Therefore, the polymer of this invention is more likely to last longer than conventional ones.

Crosslinking of the type only possible with urea linkages further increases the longevity of this product. The ratio of isocyanate to amine is selected so that there is  
 15 some excess isocyanate present. This excess then reacts with active hydrogen atoms in the initial polymer to yield biuret crosslinking. Biuret crosslinking is known to be more stable than the allophanate form of crosslinking (Szycher, M., *Szycher's Handbook of Polyurethanes*, pp. 4-9, CRC Press, Boca Raton, 1999).

Crosslinking also increases the molecular weight and reduces the free  
 20 volume of the polymer structure. The resulting structure reduces the rate of release of the active ingredient and prolongs the life of the product by reducing the rate of permeation of moisture into the structure.

Although this process is especially useful for spray systems, it can be adapted for roller coating and other coating systems. For this purpose, use of more  
 25 sterically hindered isocyanates (e.g., 2, 4'-MDI) would be desirable.

#### **Compositions Rich in Aliphatic/Alicyclic Moieties**

Many applications of this invention do not expose the product to sunlight. However, protection of utility poles, wharves, fence posts, and some parts of  
 30 buildings do expose the product to sunlight that contains significant UV radiation. Products that use MDI, TDI, and other aromatic isocyanates are likely to fail due to photo-oxidation and other free radical-initiated reactions. Aromatic isocyanates

absorb UV radiation in the range of 220 nm to 300 nm. Various UV absorbing additives could be used to alleviate this problem, especially if long product life is not a goal. However, longevity is a major goal for the products of this invention. Accordingly, polymer design can be used to increase the UV resistance of the inventive pest species control system.

### **Isocyanate Component**

Polyurethanes made from aliphatic and alicyclic isocyanates are known to resist yellowing upon exposure to sunlight because they do not absorb UV radiation, in contrast to those made with aromatic isocyanates. The preferred aliphatic isocyanates include, for example, 1,6-hexamethylene diisocyanate (HDI) and 1,4-tetramethylene diisocyanate. Preferred alicyclic diisocyanates include, for example, hydrogenated methylene diphenyl diisocyanate, 1,4-cyclohexane diisocyanate, and isophorone diisocyanate.

Longevity in all uses is enhanced by the increased hydrophobicity of the non-aromatic isocyanates. It is further enhanced if the non-aromatic isocyanates are used in a formulation that yields a product that has a low percentage of soft segments. Soft segments contribute to water absorption that reduces longevity. A soft segment in polyurethanes is defined as a portion of the polyurethane molecule that is amorphous or low in crystallinity. Such regions usually arise from the polyol component. They can be caused by use of long-chain polyol ingredients or by using shorter chains but having frequent amorphous regions. In this invention, the formulator uses short-chain polyol ingredients (e.g., polypropylene glycols with MW < 1000, preferably about 300 daltons). The formulator also limits the polyol content to less than about 20%. In some embodiments, diamines are substituted for polyols.

Soft segments not only contribute to water absorption, but also to elongation and elasticity. The longevity benefits that are attained from low soft segment content have to be balanced with the need for some flexibility in the coating product, as is true with all coatings.

### **Effects of Crystallinity and Cross-Linking**

The hard segments of the polymer chain are crystalline or crosslinked. They resist permeation by water and oxygen. This barrier attribute contributes to the longevity of the product. The barrier attribute applies also to the active ingredient so that the release rate is reduced by the presence of hard segments.

The sensitivity of the carbonyl groups in these polymers to UV radiation is reduced by the hydrogen bonding that is involved in crystalline domains of polyurethanes (Szycher, M., *Szycher's Handbook of Polyurethanes*, pp. 2-10 to 2-20, CRC Press, Boca Raton, 1999). Therefore, crystallinity enhances the longevity of the products of this invention.

The hard segments also contribute to the rigidity of the product. Because some flexibility is needed, an upper limit is set for the percentage of hard segments. There are six types of crosslinks, some of which can be broken under stress and reformed. The six types of crosslinking are:

1. Use of isocyanates with functionality greater than 2 creates crosslinks between polymer chains. A commercially available example is polymeric methylene diisocyanate (PMDI), which has an average number of isocyanate groups that is between 2 and 3. Another commercially available isocyanate with functionality greater than 2 is the product obtained by reaction of HDI with water. It has a functionality of 3.
2. Use of low molecular weight polyols with functionality greater than 2 creates tight crosslinks between polymer chains. These crosslinks are involved in generating hard segments in the polyurethane. Examples of hydroxy crosslinkers include trimethylolpropane, glycerin, and sorbitol.
3. Use of polyols with functionality greater than 2 also creates crosslinks between polymer chains. The tightness of polyol crosslinking is less than that achieved with isocyanates or low molecular weight polyols because the polyol chains are much longer. Examples of polyols with a functionality of 3 include glycerin polyether triols, and trimethylol propane polyether triols. Hydrogenated castor oil, which has a functionality between 2 and 3, is a polyester that has crosslinking capabilities.

4. In a system in which the molar equivalents of the diol are reacting with the isocyanate, there is still an opportunity for crosslinking by allophanate formation. The hydrogen of the  $-NH$  group of a urethane can react with an isocyanate group associated with another chain which forms a branching at this point. This means that a hydroxyl group somewhere in the polymer does not have an isocyanate partner. Thus, the polymer becomes crosslinked, but it also has developed some weak points where hydroxyls are not reacted. However, the formulation can be modified to have an excess of isocyanate groups above that required by stoichiometry in order to accommodate such unreacted hydroxyl groups. Then, allophanate crosslinking can be used without leaving unsatisfied hydroxyls. Use of vaporous amine catalysts would be desirable to obtain the most complete reaction of the residual hydroxyls (for example, U.S. Patent No. 4,517,222).
5. Reaction of isocyanate with water yields free amine groups, which are much more reactive with isocyanate groups, so that di-substituted urea groups are formed. These ureas also can react with isocyanate groups to form highly stable biuret groups. Thus, astute use of moisture can cross-link the polyurethane to make it more resistant in the environment. Instead of using the reaction of water with isocyanate to make the amine, it may be more desirable to manufacture the polyurea more directly as described above wherein isocyanate compounds are reacted with amine compounds, which then is added to the isocyanate cross-linkers to form polyureas. Then, the crosslinking amine need not be the one that results from reaction of the isocyanate with water.
6. Virtual Crosslinking via Hydrogen Bonding is associated with the development of hard segments. This concept allows a product to have a higher percentage of hard segments than would be possible in conventional polyurethane systems. Hydrogen bonding "virtual" crosslinks are reversible and, therefore, of value to this embodiment of the invention. The major hydrogen bonds are those between  $-NH$  and  $-C=O$  groups located in separate chains of the polymer.

### **Polyol Component**

Almost all commercial polyurethanes make use of polyols that are hydroxy-terminated polyesters or polyethers. The presence of the ester and of ether linkages facilitates the penetration of water or oxygen into the polyurethane. One embodiment of this aliphatic/alicyclic embodiment is the replacement of some or all of the polyester/polyether moieties with aliphatic and/or alicyclic moieties. For example, butadiene can be polymerized to make a polybutadiene that can be converted to hydroxy-terminated aliphatic compounds. This butadiene-derived diol then is reacted with HMDI to generate polyurethanes that are very hydrophobic (Ma, *et al.*, "Mechanical Properties of Hydrophobic Urethane Elastomers", *ACS Polymer Division Preprints*, 2000, page 380-381). These polyurethanes show considerable enhancement of barrier properties and have good modulus, even though they contain 60% to 85% of the soft segment ingredient.

The aliphatic or alicyclic polyol component of the polyurethane of this invention includes the diol described above and other diols as follows:

1. straight chain hydrocarbons that have 8 to 30 carbons with hydroxyl groups at each end;
2. carbocyclic rings that contain from 5 to 32 members with hydroxyl groups that are not on adjacent carbons; and
3. molecules that have one or more rings, as defined in item 2 immediately above, that have two straight chain hydrocarbon chains that are substituents, with two hydroxyl groups are present, one at the end of each pendent chain.

Thus in this invention, alicyclic/aliphatic isocyanates are employed in ways that generate polyurethanes with a high percentage of hard segments. Use of a limited percentage of short-chain polyols and added diamines or triamines promote crystallization and virtual crosslinks that are needed to have high percentages of hard segments without being overly rigid. The invention also includes the use of polyols that are not derived from polyesters or polyethers but which are aliphatic and/or alicyclic ingredients (U.S. Patent No. 5,043,484). The added hydrophobicity can provide much longer product life.

Two additional sources of hydroxyls for reaction with isocyanate-terminated polyurethanes are silanol and epoxy intermediates. Thus, block copolymers can be



made by reacting silanols with polyurethane prepolymers that have free isocyanate groups. Silanols have silicon atoms attached to hydroxyl groups. Epoxy resins cure to provide hydroxyl groups that are reactable with isocyanate groups. These block copolymers also have been made and found to be useful in medical devices (see  
5 Szycher, *supra*).

### **Pest Species Control Agents**

Acceptable insecticides include those insecticides approved by the U.S. Environmental Protection Agency to kill or repel termites, ants, other boring insects,  
10 and wood decaying microorganisms. The class of insecticide which is presently preferred for use in the present invention are pyrethrins, including tefluthrin, lambdacyhalothrin, cyfluthrin, deltamethrin, cypermethrin, permethrin, and natural permethrin. It will, however, be recognized by those skilled in the art that other effective insecticides such as isofenphos, fenvalerate, cypermethrin, permethrin,  
15 bifenthrin, natural pyrethrin, organophosphate type insecticides, repellents as well as naturally occurring chemicals that act as irritants such as skunk oils and extracts of pepper can also be used. These insecticides are available from a number of commercial sources such as, for example, Dow Chemical Company, Bayer, ICI Industries, Velsicol, Novartis, Syngenta, and FMC Corporation.

20 Insecticides, pesticides, pest species repellents, alone or in combination with one and another, or in combination with other bioactive ingredients, such as fungicides, may also be used in accordance with the present invention. Combinations of insecticides, pesticides, repellents, nematicides (also referred to as nematocides), and fungicides additionally may be used to advantage. Fungicides  
25 include, for example, carboximide, dicarboximide, diflumetorim, ferimzone, chloropicrin, pentachlorophenol, tri-chloronitromethane, 1-3 dichloropropane, and sodium N-methyl dithiocarbamate. Nematicides include 1,3 dichloropropene, ethoprophos, fenamiphos, benfuracarb, and cadusafos.

Commercial molluscicides include, *inter alia*: Niclosamide (Bayluscide) from  
30 Bayer; Clamtrol from Betz; Calgon H-130 from Calgon, and Mexel 432 from RTK Technologies. These products are intended for controlling Zebra Mussels that cause water intake problems for electric power plants and/or the snails that carry

Schistosomiasis. Copper compounds, e.g., cuprous oxide, have been a favorite leachable component of antifouling paints. Insoluble cuprous chelates could be active ingredients that bloom to the surface and stay there repelling fouling organisms. Commercial antifouling paints (e.g., SIL MAR) that feature silicone ingredients make the surface too slippery for fouling organisms to form a stable biofilm. Organotin compounds are known to work, but present toxicity issues. Copper compounds are seen to present toxicity issues too. Organic antifouling agents, such as are disclosed in U.S. Patent No. 5,441,743, may be used to advantage too. Endod, a natural plant extract from the soapberry bush, contains saponin and lemmatoxin. Endod has been used to control Zebra and Quagga Mussel infestations.

#### **Application of the Pest Species Control Agent**

Catalysts also may be added to some of the polyurethane systems to lower the reaction temperature down to levels more easily tolerated by the pesticide, in addition to accelerating the curing process. For example, a suitable catalyst may drop the reaction temperature of polymerization from about 160° C to about 120° C. Suitable catalysts include homogeneous and heterogeneous catalysts. Heterogeneous catalysts are usually provided as fine powders. Examples of suitable catalysts include, for example, tertiary amines, organometallic tin compounds, triethylene diamine, dibutyl tin dilaurate, dibutylbis(laurylthio)stannate, dibutyltinbis(isooctylmercapto acetate), dibutyltinbis(isooctyl maleate), dimethylcyclohexylamine, and 1,8-diazabiscyclo[5,4,0]undec-7-ene (DBU). Often, these catalysts are not added to the transport polyurethane ingredients until just before application.

To combine the sustained release product with the low temperature catalytic curing agent in a single application (e.g., spray application), the two are mixed together immediately prior to spraying, to prevent the clogging of the spray equipment. Preferably, the curing agent is combined with the sustained release product within the nozzle of a pressurized spraying device. However, applications wherein the sustained release product is combined with a low temperature catalytic

curing agent prior to the introduction of the mixture into the spraying device are within the scope of the invention.

A great variety of suitable spraying devices are suitable for the practice of the present invention. For example, pages 158-170 of Oertel's, *Polyurethane Handbook*, published by Hanser in 1993 describe a variety of suitable mixheads. These devices are well understood by those having skill in the art, and no further elaboration of their operation is necessary to enable their use in the practice of the present invention. As contemplated by the present invention, any spraying device which will allow a liquid to be combined with pressurized gas (typically air) and expelled as a fine mist or droplet is acceptable, as are spraying devices which allow the delivery of liquid under pressure without air.

The beads preferably are small enough to fit through the spray head of standard spraying equipment utilized in the spray application of the present invention, and comprise the same pesticide bound within transport polymer matrix.

It will be appreciated, however, that the versatility of the invention permits application by other techniques including, for example, roller coating, brush coating, dipping, spray curtains, and like conventional application techniques.

The coatings thus formed by the practice of the present invention will immediately begin releasing pesticide in sufficient quantities to deter the invasion of pest species through the barrier formed by these coatings. These coatings will also continue to release pesticide in sufficient quantities to deter the invasion of pest species for many years, in some cases for periods of thirty years or greater.

To enhance the safety of these coatings, a protective layer of ethylene vinyl acetate (EVA), polyvinyl alcohol (PVA), or a like material may also be applied thereover. The EVA also may be applied as a sprayed coating utilizing spray equipment well known by those having skill in the art. The EVA is applied in a second spraying on top of the polyurethane coating. The EVA coating provides a protective barrier to prevent humans and other non-target animals from coming into contact with the pesticide being released from the coating. The EVA coating also assists in enhancing the durability of the coating through its resistance to the effects of UV radiation.

In addition to EVA and PVA coatings, polyvinyl acetate latex coatings can be applied to the cured urethane product, using spray technologies employed to paint the interior of buildings. Copolymers of vinyl acetate with acrylic esters also are used to make latices that are promising for spray application. Styrene butadiene latex  
 5 paints also can be spray-applied to protect humans from contact with the pesticide.

While the invention has been described with reference to certain preferred embodiments, those skilled in the art will understand that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to  
 10 adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims. In this application all units are in the  
 15 metric system and all amounts and percentages are by weight, unless otherwise expressly indicated. Also, all citations referred herein are expressly incorporated herein by reference.

20

## EXAMPLES

Various clay carriers were evaluated to determine their capacity to adsorb  
 25 and retain pesticide, and their capacity to thereafter release the pesticide.

### Clays

- (1) Attapulgus clay (ATTP)
- (2) Montmorillinite (bentonite) clay
- (3) Nanoclays from Nanocor, Inc. (de-ionized montmorillonite, and amine  
 30 functions added for polymer use)
  - (a) Nanomer I.30E
  - (b) Nanomer I.30P
  - (c) Nanomer I.34TCN
  - (d) Nanomer I.44PA
  - 35 (e) Nanomer PGV

# HOLDING CAPACITY

Each tested active agent was simply slow-blended into the clay using a Hobart mixer. Active agents that were solid at room temperature were pre-melted, the clay heated, and the heated ingredients mixed by the same procedure. The following results were recorded:

TABLE 1

CLAY	ACTIVE AGENT	HOLDING CAPACITY <sup>(1)</sup>	STATUS <sup>(2)</sup>
ATTP			
02-76-M	Dimethyl succinate	0.5	Watery
02-76-N	Diethyl adipate	0.48	
02-76-P	1-decanol	0.43	
02-76-Q	2-methyl hexanoic acid	0.42	
02-76-R	1,4-heptadienal	0.39	
02-76-S	Permethrin	0.45	NC
02-76-T	Cypermethrin	0.47	NC
02-76-U	Fenvalerate	0.48	NC
02-76-X	Bifenthrin	0.45	NC
Bentonite			
02-81-M	Dimethyl succinate	0.52	Watery
02-81-N	Diethyl adipate	0.48	
02-81-P	1-decanol	0.46	
02-81-Q	2-methyl hexanoic acid	0.39	
02-81-R	1,4-heptadienal	0.38	

02-81-S	Permethrin	0.46	NC
02-81-T	Cypermethrin	0.5	NC
02-81-U	Fenvalerate	0.42	NC
02-81-X	Bifenthrin	0.48	NC
02-81-Z	Trifluralin	0.41	
Nanocor N I.34TCN			
02-87-M	Dimethyl succinate	0.67	
02-87-P	1-decanol	0.62	
02-87-S	Permethrin	0.52	
02-87-X	Bifenthrin	0.51	
02-87-Z	Trifluralin	0.39	
Nanocor N I.44PA			
02-87-Z	Trifluralin	0.37	
Nanocor N I.30E			
02-88-M	Dimethyl succinate	0.69	
02-8-N	Diethyl adipate	0.27	
02-88-P	1-decanol	0.27	
02-88-S	Permethrin	0.53	
02-88-V	Nonanol	0.55	
02-88-X	Bifenthrin	0.55	
02-88-Z	Trifluralin	0.46	
Nanocor N I.30P			

02-89-M	Dimethyl succinate	0.69	
02-89-N	Diethyl adipate	0.51	
02-89-P	1-decanol	0.61	
02-89-S	Permethrin	0.56	
02-89-V	Nonanol	0.55	
02-89-X	Bifenthrin	0.53	
02-89-Z	Trifluralin	0.42	
Nanocor PGV			
02-90-M	Dimethyl succinate	0.45	NC
02-90-P	1-decanol	0.32	
02-90-S	Permethrin	0.4	Watery
02-90-V	Nonanol	0.46	Watery
02-90-X	Bifenthrin	0.41	NC
02-90-Z	Trifluralin	0.44	Watery

- (1) Gm active/gm active+clay (e.g., 1/1 = 0.5, 2/1=0.66, 3/1=0.75, 4/1= 0.8)
- (2) No status indicates good mix and swell of clay.  
 NC is no expansion of clay.  
 Watery is when the active compound does not swell the clay.

5

The following table lists the average adsorption for the various clays is as follows (the N I.44PA was ignored as only 1 active agent was tested) and the percentage increase of the nano-clays over the standard clays.

TABLE 2

CLAY TYPE	AVERAGE ADSORPTION	% INCREASE OVER ATTP	% INCREASE OVER BENTONITE
ATTP	0.452	--	--
Bentonite	0.410	--	--
N I.34TCN	0.542	19.9	32.20
N I.30E	0.474	4.87	15.61
N I.30P	0.553	22.3	34.88
PGV	0.413	- 8.63	0.73

Thus, the above-tabulated results indicate that the nano-clays unexpectedly have the capacity to adsorb more active agent than conventional clays. This is especially unexpected considering the wide variety of active agents tested. When the release rate data below is reviewed, the superiority of nano-clays to standard clays will be complete.

#### POLYMER COMPATIBILITY

A series of thermoplastic and thermoset materials were compounded with the pesticide adsorbed clay compositions and tested for their release rates. Lower release rates are preferred in order to extend the active life of the pesticidal composition. The following data was recorded.

#### Thermoplastics

For compounds with low vapor pressures, *i.e.*, pesticides, extrusions heated to 300° C were performed with the actives loaded onto clays.



Trifluralin Study

TABLE 3

SAMPLES	CLAY	RELEASE RATE ( $\mu\text{G}/\text{CM}^2/\text{DAY}$ )	% DECREASE OVER ATTP
Polyethylene (MA 778-000)	ATTP	17.49	--
Polyethylene (MA 778-000)	PGV	12.5	28.5
Polyethylene (MA 778-000)	I.44PA	11.47	34.4
Polyethylene (MA 778-000)	I.30P	7.73	55.8
Polypropylene (MU 763-00)	ATTP*	--	--
Polypropylene (MU 763-00)	PGV	0.9	--
Polypropylene (MU 763-00)	I.44	1.07	--
Polypropylene (MU 763-00)	I.30P	0.41	--

\* Bad mixing/Extrusion

5

These results again demonstrate that the nano-clays unexpectedly yield lower release rates compared to standard clays. The extent of such lower yield rates can be seen to range from over 28% up to over 55%. At stated above, the increased adsorption capacity coupled with slower release rate makes the use of nano-clays for pesticide applications unexpected and unique.

10

Thermoset Urethane

The following urethane thermosets that contain N I.30E nanoclay were evaluated:

15

- (a) Uniroyal Solithane S113, C1134 and TIPA; and S113, and Cognis 115 or 253.
- (b) Devcon Flexane 80

TABLE 4\*

SAMPLE	POLYMER	ACTIVE AGENT	MIX/SET	RELEASE RATE ( $\mu\text{G}/\text{CM}^2/\text{DAY}$ )
02-79-M	Solithane/Urethane	Dimethyl succinate	Good	11
	F80 Urethane	Dimethyl succinate	Excellent	22
02-79-N	Solithane/Urethane	Diethyl adipate	Marginal	14
	F80 Urethane	Diethyl adipate	Good	16
02-79-P	Solithane/Urethane	1-decanol	Poor	31
	F80 Urethane	1-decanol	Good	28
02-79-V	Solithane/Urethane	1-Nonanol	Poor	25
	F80 Urethane	1-Nonanol	Good	19
02-79-S	Solithane/Urethane	Permethrin	Good	5.7
	F80 Urethane	Permethrin	Good	5.9
03-11-X	Solithane/Urethane	Bifentrin	Good	3.2
	F80 Urethane	Bifentrin	Good	4.5
03-11-T	Solithane/Urethane	Cypermethrin	Good	6.5
	F80 Urethane	Cypermethrin	Good	7.9
03-11-U	Solithane/Urethane	Fenvalerate	Good	6.1
	F80 Urethane	Fenvalerate	Good	6.4

\* Release rates measured with wipes of surfaces over 6-month period; active loading was set 10% parts by weight. Release rates mimic vapor pressures, high release:high Vp

5

The F80 systems (Table 4) were the exception because they have an amine catalyst that does not react with the active agents that contain ester groups. Such systems, then, do provide a good release platform.